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SHORT COMMUNICATION

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible.*

Acta Cryst. (1985). C**41**, 157–158

Structures of a hydrocarbon $C_{58}H_{40}$ and its photo-oxidation products. I. 1,1,2,3,4,5,6-Heptaphenyl-1,4-dihydrobenz[*e*]-*as*-indacene – a new determination.

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Abstract

$M_r = 736{\cdot}95$, triclinic, $P\bar{1}$, $a = 11{\cdot}903$ (4), $b = 18{\cdot}433$ (6), $c = 10{\cdot}035$ (4) Å, $\alpha = 107{\cdot}05$ (3), $\beta = 95{\cdot}42$ (3), $\gamma = 98{\cdot}76$ (3)°, $V = 2058$ (2) Å^3, $Z = 2$, $D_x = 1{\cdot}190$ Mg m^{-3}, Cu $K\alpha_1$, $\lambda = 1{\cdot}5404$ Å, $\mu = 0{\cdot}528$ mm^{-1}, $F(000) = 776$, $T = 295$ (2) K, $R = 0{\cdot}043$ for 5993 observed data [$I > 3\sigma(I)$], 0·068 for all 7823 data. The sample was provided by M. J. Gallagher and I. D. Jenkins of the School of Chemistry, the University of New South Wales. With a different set of reflection data and a different unit cell, the molecular structure essentially agrees with that determined independently by Shoja, Espiritu, White & Borowitz [*Acta Cryst.* (1980), B**36**, 1967–1969].

Introduction

The molecular structure of this hydrocarbon $C_{58}H_{40}$ (I) (Fig. 1) and those of two isomeric photo-oxidation products (II) and (III) of formula $C_{58}H_{40}O_2$, referred to as (*B*) and (*A*) respectively by Gallagher & Jenkins (1969, p.2613), who prepared all three, could not be determined by chemical means. The structure of (II) has been solved by diffraction methods (Grainger, 1984). Work on (III) continues.

Shoja, Espiritu, White & Borowitz (1980) (hereafter Shoja) and this study have independently found essentially the same structure for (I), and complement one another in regard to the accuracies of determining the unit cell and atomic coordinates.

Experimental

Tabular crystal 0·5 × 0·3 × 0·15 mm; Ni-filtered Cu radiation; Siemens AED diffractometer; $(\sin\theta)/\lambda$ to 0·61 Å^{-1}; absorption correction on 64-point grid; 7823 unique reflections measured, 1830 unobserved [$I < 3\sigma(I)$]; $h = -14$ to 14, $k = -22$ to 21, $l = 0$ to 12. Intensity statistics indicated $P\bar{1}$. Structure solved by direct methods (*MULTAN*80), refined on $|F|$ by blocked-matrix least squares (one block each for the 7 phenyl rings and another for the remaining parameters) on 'observed' data; H atoms in calculated positions at 1·0 Å with temperature parameters set equal to those of bonded atoms; refined scale factor, isotropic extinction correction parameter, positional and anisotropic thermal parameters for non-hydrogen atoms (524

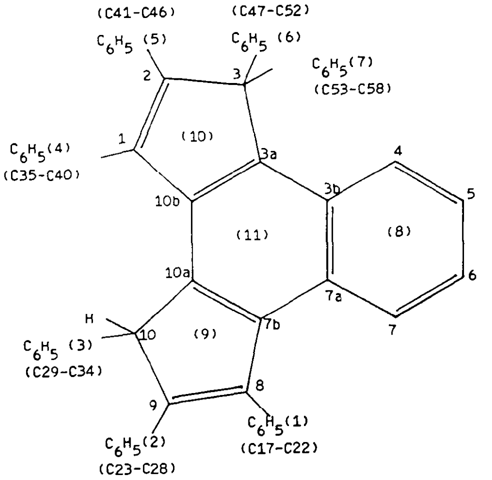

Fig. 1. Structural formula and atomic labels for the hydrocarbon $C_{58}H_{40}$. (Note that the crystallographic numbering differs from that used in the title.)

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parameters); weights based on counting statistics; final R and R_w 0·068 and 0·053 for all 7823 data, 0·043 and 0·042 for 5993 observed data; $S = 3{\cdot}77$; Δ/σ for positional parameters in final cycle max. 0·83, r.m.s. 0·16. Max. and min. electron densities in final difference Fourier synthesis 0·20 and $-0{\cdot}19$ e Å^{-3}. Final extinction parameter $R = 1{\cdot}339 \times 10^{-4}$ (a small value) where corrected value is given [Larson, 1970, equations (21) and (11)] by

$$|F_c|^* = k\,|F_c|\,[1 + 2R\bar{T}\gamma\,|F_c|^2]^{-1/4},$$

$$\text{where} \qquad \gamma = \frac{1 + \cos^4 2\theta}{\sin 2\theta(1 + \cos^2 2\theta)},$$

$\bar{T}$ = effective path length (cm), k = scale factor, $|F_c|$ is uncorrected value. Scattering factors for C were 'HF' values in *International Tables for X-ray Crystallography* (1974), p.72), with correction $f' = 0{\cdot}017$, and for H tabulated value (*International Tables for X-ray Crystallography,* 1974). Principal computer programs *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), *BLOCKLS*, a much-modified *ORFLS* (Busing, Martin & Levy, 1962), *FANDEB*, derived from *ORFFE* (Busing, Martin & Levy, 1964) and *ORTEP* (Johnson, 1976).

The intensity data set was collected in the year 1971 and the structure was finally solved by *MULTAN*80, which succeeded on the first run, the E map showing all non-H atoms. A subsequent check on the relevant set of *FASTAN*-refined phases (which had exceptionally good figures of merit) showed there were 431 correct phases, 0 incorrect and 34 undetermined.

Discussion

The refinement described above gave a much lower R factor and smaller e.s.d.'s in the atomic parameters than those of Shoja despite the use of group-blocked matrix refinement as against simple block-diagonal. The resulting coordinates are presumably more accurate than those of Shoja.

On the other hand, the lattices defined by the Shoja unit cell (S cell) and the one above (G cell) differ significantly. The S cell, derived by a least-squares fit using 15 high-angle reflections on a modern diffractometer, should be more reliable than the G cell for which 9 manually-centred reflections were used without a least-squares fit, the e.s.d.'s being *a priori* estimates.†

Thus for calculating molecular geometry probably the most accurate procedure is to employ the fractional atomic coordinates given herein together with a modified G cell (the G' cell), which accords with the lattice defined by the S cell. The required axial vectors $\mathbf{a}'$, $\mathbf{b}'$ and $\mathbf{c}'$ are found to be $\mathbf{b}$, $-(\mathbf{a}+\mathbf{c})$ and $\mathbf{a}$, respectively, in terms of the S cell. The G' cell has $a' = 11{\cdot}916$ (2), $b' = 18{\cdot}468$ (4), $c' = 10{\cdot}041$ (2) Å, $\alpha' = 106{\cdot}98$ (2), $\beta' = 95{\cdot}44$ (2), $\gamma' = 99{\cdot}01$ (2)°. (The magnitudes of $\mathbf{a}+\mathbf{c}$ and $\mathbf{c}$ differ by only 0·204 Å.) Neither of the above is the reduced cell, which is all-acute angled and has axes $\mathbf{a},-\mathbf{b},-\mathbf{c}$ in terms of the S cell. The atomic coordinates herein are (ideally) calculable in terms of the Shoja coordinates as y, $1-z$, $0{\cdot}5+x-z$.

Bond lengths* based on the atomic coordinates determined using (*a*) the G cell and (*b*) the G' cell have been compared with each other and with those listed by Shoja (*c*). Of 68 bond lengths listed, taking combination (*b*) as reference, one finds significant differences in the other columns. In 18 cases in (*a*) the bond length differs by amounts ranging from σ_b to $3\sigma_b$ (0·002 to 0·006 Å). In (*c*) there are 47 cases of differences between σ_b and $6\sigma_b$ (0·002 to 0·017 Å).

The small corrections made by using the G' cell instead of the original G cell are worthwhile as the error on average tends to shorten the bonds.

Finally, it should be said that however the geometry is calculated the conclusions of the Shoja paper about this structure still stand.

Thanks are due to Professor M. J. Gallagher (School of Chemistry, The University of New South Wales) for suggesting the problem, for providing crystals and for helpful discussions; to D. C. Craig for data collection and assistance in computing; and to the University for computing time on the CDC-171.

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† Crystals are not now available to re-measure the G cell.

* Lists of structure factors, anisotropic thermal parameters, fractional atomic coordinates of all atoms, comparison of bond length calculations, bond angles and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39784 (42 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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